

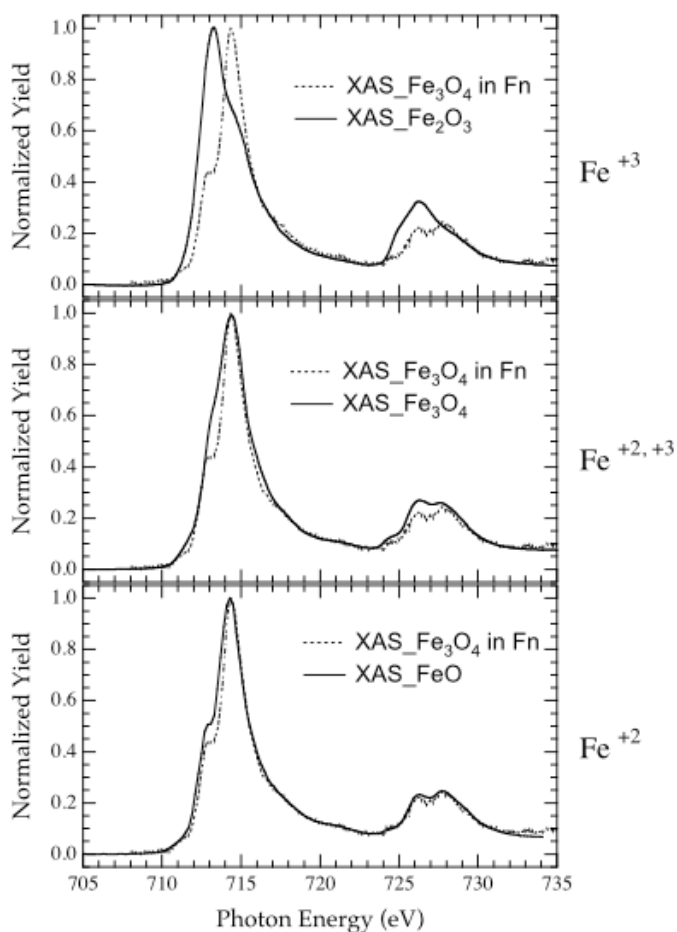
Identification of Fe Valence in Iron Oxide Nanoparticle Encapsulated in Protein Cages

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Introduction: There is considerable interest in the controlled formation of size constrained and nanophase inorganic materials for a variety of technological applications such as magnetism, semiconductors, ceramics, and medical diagnostics. However, conventional solution methods often produce materials having a range of particle sizes. Since the properties of nanophase materials are intimately related to their dimensions, this implies a heterogeneity of physical properties; this heterogeneity limits their usefulness. Alternative syntheses using a biomimetic approach have utilized organized molecular assemblies for materials synthesis, such as micelles, microemulsions, surfactant vesicles, Langmuir monolayers (and multilayers) and the protein cage of the iron storage protein ferritin. All these have proven to be versatile reaction environments and a wide range of inorganic materials have been synthesized using these systems. However, there are severe limitations to these systems. Micelles for example are dynamic structures with fluctuations in size, whereas vesicles often have limited stability with regard to aggregation and hydrolysis. Extremely tight size distributions for single crystal magnetic nanoclusters can be obtained by bio-mineralization of protein cage structures. Target nanocluster size and shape can be varied by selection and/or genetic engineering of protein complex to use as the template. Complete variability in magnetic alloy concentration can also be introduced.

Comparison of Fe XAS spectra for iron oxide nanoclusters in ferritin



Methods and Materials: We have generated a library of uniform size clusters by the biomineralization process for template-constrained synthesis of iron oxide nanoparticles. Nanomagnetic cluster synthesis is performed by the utilization of protein cages in highly monodisperse sizes ranging from 5 to 24 nm ID as mineralization templates for the preparation of highly uniform metal oxide particle cores. These oxide cores can be later reduced to yield the corresponding monodisperse metal particles. To examine the valence of the Fe, we have used X-ray absorption spectroscopy on 5 nm Fe_3O_4 single crystal nanoclusters. Other structural studies confirm the stoichiometry and structure of these small clusters.

Results: The XAS spectra of the Fe $L_{2,3}$ edge for (nominally) Fe_3O_4 5 nm nanoclusters synthesized in ferritin cages is displayed in the figure at left. For comparison, we show XAS spectra for thin films of Fe_2O_3 , Fe_3O_4 , and FeO where the valence of the Fe is +3, mixed (+2 and +3), and +2, respectively. The iron in the iron oxide nanoparticles has a spectrum nearly identical to the FeO thin film.

Conclusions: The similarity of the Fe XAS spectra suggests that the high surface to volume ratio present in the 5 nm magnetic iron oxide clusters alters the electronic structure of the oxide.

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